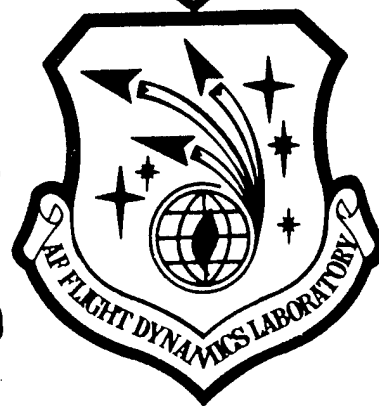# AIR FORCE FLIGHT DYNAMICS LABORATORY
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AIR FORCE SYSTEMS COMMAND
WRIGHT PATTERSON AIR FORCE BASE OHIO

DETERMINATION OF A NITRIC OXIDE VIBRATIONAL
RELAXATION RATE FROM ELECTRON BEAM
MEASUREMENTS IN HIGH ENTHALPY EXPANSION FLOWS

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June 1974

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TECHNICAL MEMORANDUM AFFDL-TM-74-120-FXN

NOTICE

FOREWORD

This Technical Memorandum presents the results of a theoretical correlation of electron-beam vibrational temperature measurements of Nitric Oxide performed in the 2 Ft Electrogasdynamics Facility. The data has been examined and correlated and a NO vibrational relaxation rate, valid for high enthalpy, low density air flows, has been deduced. It has been found that a relaxation rate between 5 and 30 times the NO shock-tube rate deduced by Wray correctly predicts the NO vibrational temperature.

This report was prepared by S. S. Lazdinis of the R&D Group of the Experimental Engineering Branch. It is part of an Air Force Flight Dynamics Laboratory in-house research effort under work unit number 14260123, titled "Correlation of Thermochemical Diagnostic Data and Theory Related to Aerothermodynamics of High Speed Military Vehicles," Task Number 142601, and Project Number 1426. It covers work conducted between December 1973 and March 1974.

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This Technical Memorandum has been reviewed and is approved.

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SECTION I

INTRODUCTION

During a recent entry into the 2 Ft Electrogasdynamics Facility, Professor S. L. Petrie of the Ohio State University, as part of an Air Force contract, performed electron-beam measurements of the vibrational temperature of Nitric Oxide.[1] Since these measurements were the first NO vibrational temperature measurements obtained in arc-generated high enthalpy expansion flows, they have been examined in detail to determine their degree of agreement with vibrational temperature predictions based on a NO vibrational rate deduced from shock-tube experiments. The analysis has been carried out using a recently developed computer program which couples nonequilibrium chemistry with the finite rate vibrational relaxation of diatomic species in high enthalpy air.[2] This study is a companion effort to a similar investigation which deduced a value for the vibrational relaxation rate for O_2 under similar arc-tunnel conditions.[3] The results of both studies, together with results for N_2 obtained previously,[4] are a preliminary attempt at a complete description of the behavior of the vibrational relaxation of the major diatomic constituents in the test flows of arc facilities such as the 2 Ft EGF.

Although numerous experimental studies have been performed to determine the vibrational relaxation rate of NO^{5-8}, none of these efforts has duplicated the extreme conditions of pressure, temperature, and Mach number that are typical of arc tunnel flow environments. In view of the fact that N_2 vibrational relaxation rates obtained from shock-tube, i.e., normal shock, experiments have been found to differ appreciably from rates determined from

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expansion flow studies,[9] it was felt necessary to investigate whether known NO rates which were also derived from normal shock experiments would be useable in expansion flow environments. An oxygen vibrational relaxation rate deduced by the author from electron-beam measurement taken in the 2 Ft EGF has been found to agree quite closely with the value of a shock-tube rate suggested by Parker[10], falling between 1/5 and 1/2 of his value.

SECTION II

ANALYSIS

To completely describe high enthalpy, rapidly expanded nonequilibrated air flow, in addition to equations taking into account the flow chemistry, continuity, momentum, and energy, an equation specifying the behavior of the vibrationally relaxing species is also required. In this study the Landau-Teller rule, with an experimentally determined vibrational relaxation time, T_j, has been applied to calculate the vibrational temperature distribution of the major diatomic species present in the flow. The expression is given by

$$\frac{dT_v^j}{dx} = \frac{E_v^j(T) - E_v^j(T_v^j)}{uT_j}$$

where T_v^j is the vibrational temperature of species j, T is the gas static temperature, $E_v^j(T)$ and $E_v^j(T)$ are the vibrational contributions to the species enthalpy evaluated at the static and species vibrational temperatures, respectively, u is the flow velocity and $C_{p_j}^v$ is the specific heat due to purely vibrational effects.

The Nitric Oxide vibrational temperature distributions through the nozzle for the high enthalpy conditions investigated were calculated with a computer program which couples the vibrational relaxation of the diatomic air species with finite rate chemistry. Since the vibrational relaxation of N_2, O_2, NO and NO^+ was included in the analysis, the flow was characterized by four vibrational temperatures and the gas static temperature.

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Contributions from the vibrational energy mode of each diatomic species to thermochemical parameters such as the species enthalpy, specific heat, and chemical potential were calculated using the simple harmonic oscillator model evaluated at the local value of each species vibrational temperature.[2] Due to the extremely rapid equilibration of the rotational modes, the rotational temperatures of all the diatomic species were set equal to the gas static temperature. Any nonequilibrium electronic excitation effects on the flow thermochemistry were neglected because of the low gas static temperature. All electronic contributions to the thermodynamic variables were evaluated at the gas static temperature.

The Sebacher Correlation,[11] determined from numerous expansion flow studies of N_2 vibrational relaxation, was used for the vibrational relaxation rate of N_2, while the O_2 rate used was that determined by the author and is given in Reference 3. The rate for Nitric Oxide was deduced by changing the constant pre-exponential multiplicative factor in the experimentally determined shock-tube rate given by Wray in Reference 8 until the value of the computer calculated NO vibrational temperature agreed with the electron-beam measurements of Reference 1. Due to the lack of vibrational relaxation data for NO^+, its vibrational relaxation rate was set equal to the NO rate. Because of the small concentration of NO^+ for the pressure and enthalpy conditions investigated, this assumption was felt to be quite accurate and to have an insignificant effect on the values of any other parameters calculated in the analysis. Table I gives the values of the various vibrational relaxation rates used in the computer program.

TABLE   I

VIBRATIONAL RELAXATION RATES FOR

AIR SPECIES USED IN THE

COMPUTER PROGRAM

(ATM - SECS)

$(\tau p)N_2 = 3.0 \times 10^{-10} \exp[181/T^{1/3}]$

$(\tau p)O_2 = 3.4 \times 10^{-11} \exp[133.4/T^{1/3}]$

$(\tau p)NO^{WRAY} = 4.86 \times 10^{-9} \exp[(1.37 \times 10^5/T)^{1/3}]$

$\tau_{NO} = \tau_{NO^+}$

The chemical model for air used in the computer program is fully discussed in Reference 2 and will not be given here. It consists of eleven reactions and eight species and has been found adequate in predicting high enthalpy air flow conditions in the 2 Ft EGF.[4]

SECTION III

RESULTS

NO vibrational temperatures were determined by spectrographically analyz-
ing electron-beam induced radiation from the NOγ system. The measurements
were performed for arc-tunnel conditions characterized by reservoir pressures
of 350 and 500 psi, reservoir enthalpies between 2127 and 3694 Btu/lbm, and
nominal Mach numbers between 8 and 10. The temperatures were measured at
inviscid core, nozzle exit area ratios of 240 and 1740 which were produced by
the 7 1/2 and 19 inch conical nozzles, respectively. A detailed discussion of
the experimental setup of the spectrographic equipment and a detailed analysis
of both the electron-beam data and arc-tunnel operating conditions may be
found in Reference 1.

Although the accuracy of the electron-beam NO vibrational temperature mea-
surements is expected to be within 20%, the experimental electron-beam data
falls into two groups.[1] One set of data points is found to cluster about a
NO vibrational temperature to reservoir temperature ratio of 0.4 while the other
falls near a ratio of 0.25. Although the reason for this grouping is presently
unclear, a possible cause might be the NO shuffle reactions affecting the NO
vibrational population distributions.[2] Because these fast reactions are sensi-
tive functions of temperature, they might depend on various arc-tunnel para-
meters. The influence of these factors on these reaction rates and the pre-
sently employed chemical model will be investigated in the future.

Figure 1 shows how various values for the NO vibrational relaxation rate
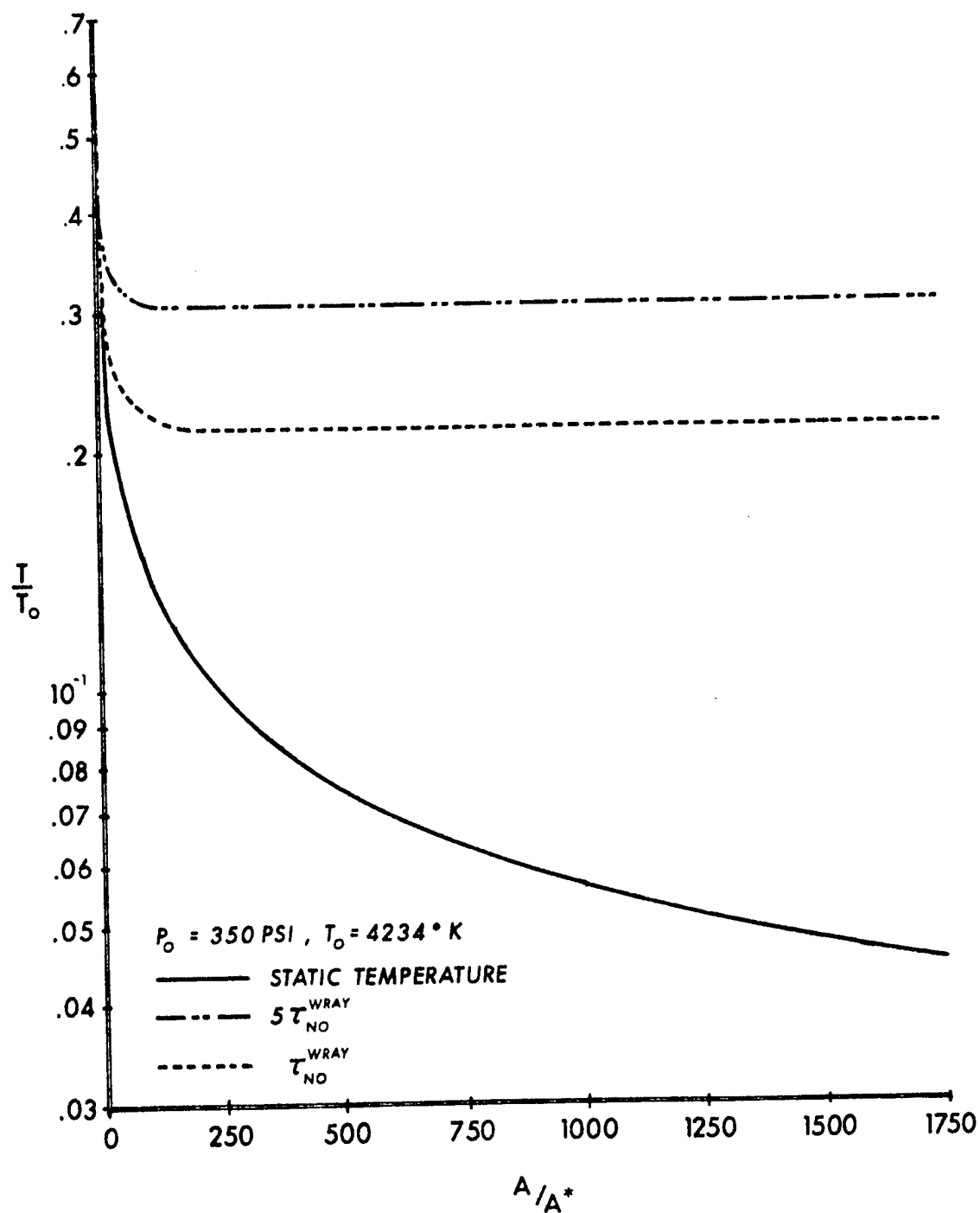affect the calculated NO vibrational temperature and gas static temperature

FIGURE 1.   BEHAVIOR OF NO VIBRATIONAL TEMPERATURE AND GAS STATIC TEMPERATURE
AS A FUNCTION OF NO VIBRATIONAL RELAXATION RATE AND AREA RATIO

distributions through the nozzle. The figure refers to a typical 2-Ft EGF run condition and is characterized by a reservoir enthalpy of 2885 Btu/lbm and a reservoir pressure of 350 psi. The NO vibrational temperatures are seen to freeze at a constant value a short distance downstream of the nozzle throat, regardless of the rate used. This behavior is similar to that observed for both N_2 and O_2. In addition, because the amount of energy trapped in the NO vibrational energy mode is very small compared to the flow enthalpy it is seen that changes in the NO vibrational relaxation rate have very little effect on the static temperature distribution.

Figures 2 through 5 compare the electron-beam determined NO vibrational temperatures at the two exit area ratios with calculated values for four different runs. The observed increase in the NO vibrational temperature with distance from the nozzle centerline is caused by the nozzle boundary layer. This behavior is similar to that of O_2 vibrational temperature but opposite to that of N_2. The latter vibrational temperature is found to decrease as the boundary layer is approached.[4] The electron-beam data are seen to be well approximated by the calculations if NO vibrational relaxation rates between 5 and 30 times the shock-tube rate, a determined by Wray[8], are used. Because these preliminary measurements provide the only NO vibrational temperature data in an expanding flow available at this time, better estimates for a NO vibrational relaxation rate valid -for arc-tunnel flows conditions different from those investigated cannot be deduced until more measurements are performed.

Figure 6 and 7 compare the calculated vibrational temperature distributions- using the best deduced value for T_{NO} for each run from Figures 2 - 5.
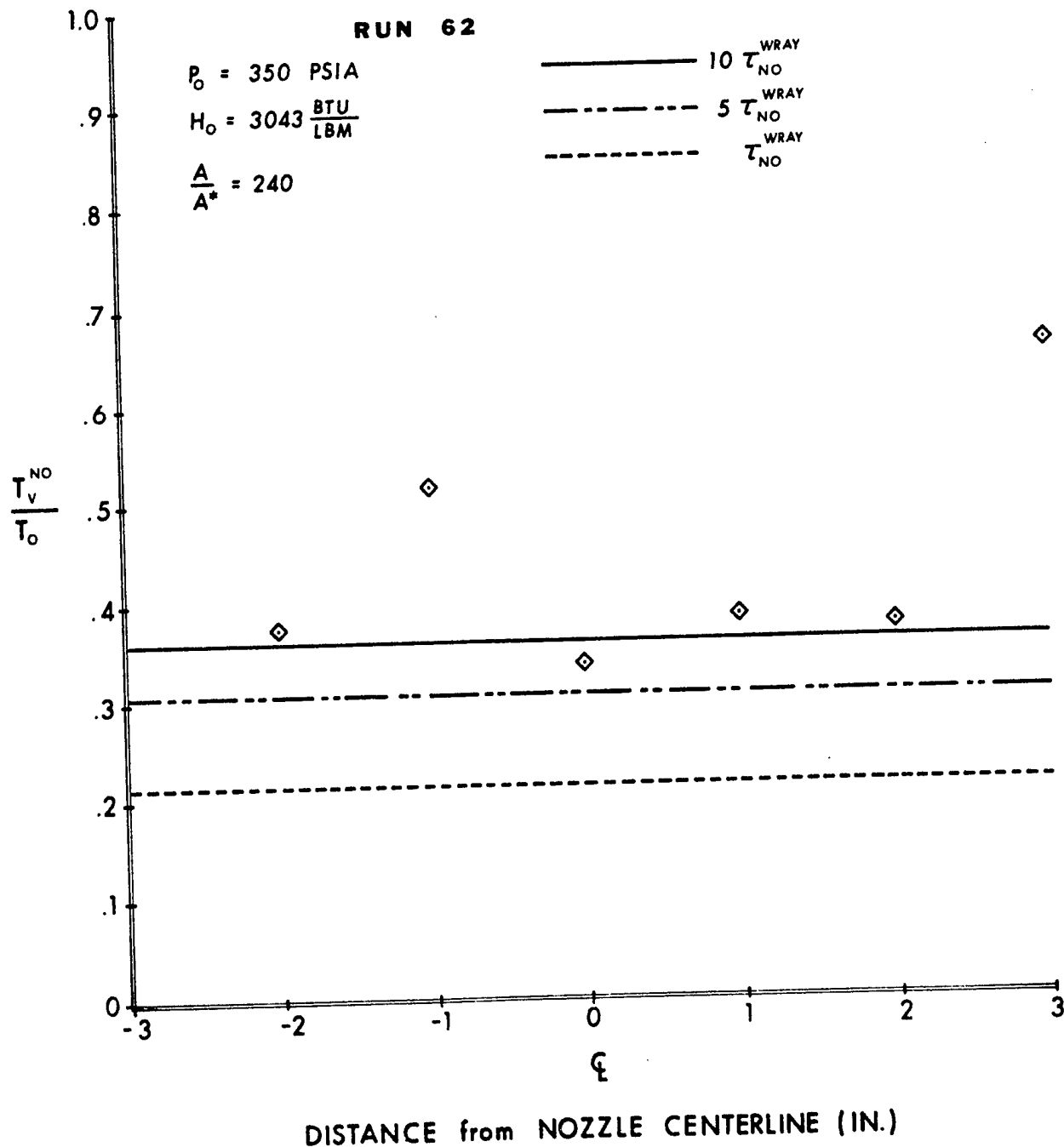
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FIGURE 2. COMPARISON OF NO VIBRATIONAL TEMPERATURE DATA WITH NONEQUILIBRIUM
CALCULATIONS (T_O = 4356°K, P_O = 350 psia, A/A* = 240)

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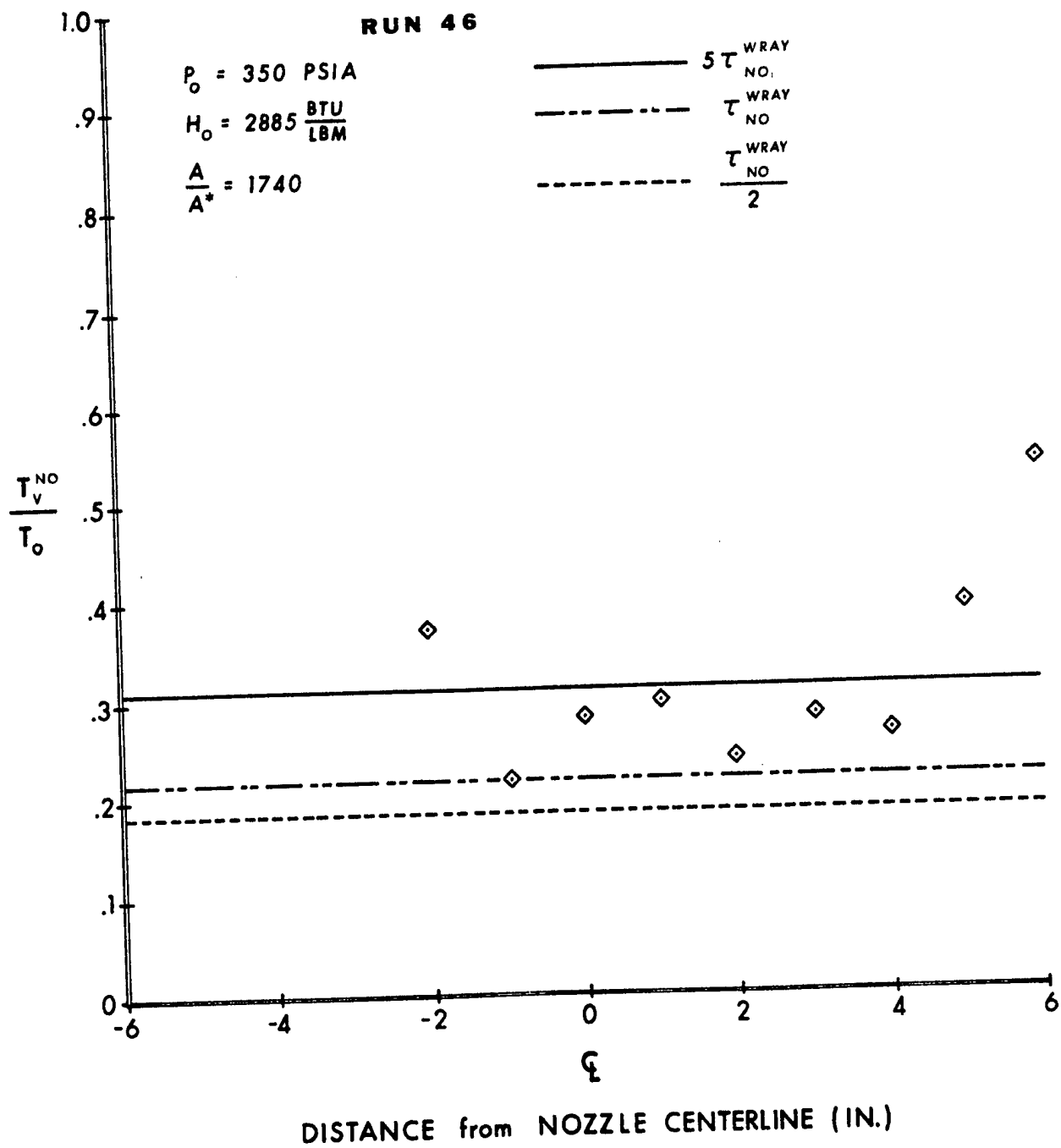
FIGURE 3. COMPARISON OF NO VIBRATIONAL TEMPERATURE DATA WITH NONEQUILIBRIUM CALCULATIONS (T_o = 4234°K, P_o = 350 psia, A/A* = 1740)

FIGURE 4. COMPARISON OF NO VIBRATIONAL TEMPERATURE DATA WITH NONEQUILIBRIUM CALCULATIONS (T_O = 4946°K, P_O = 500 psia, A/A* = 240)
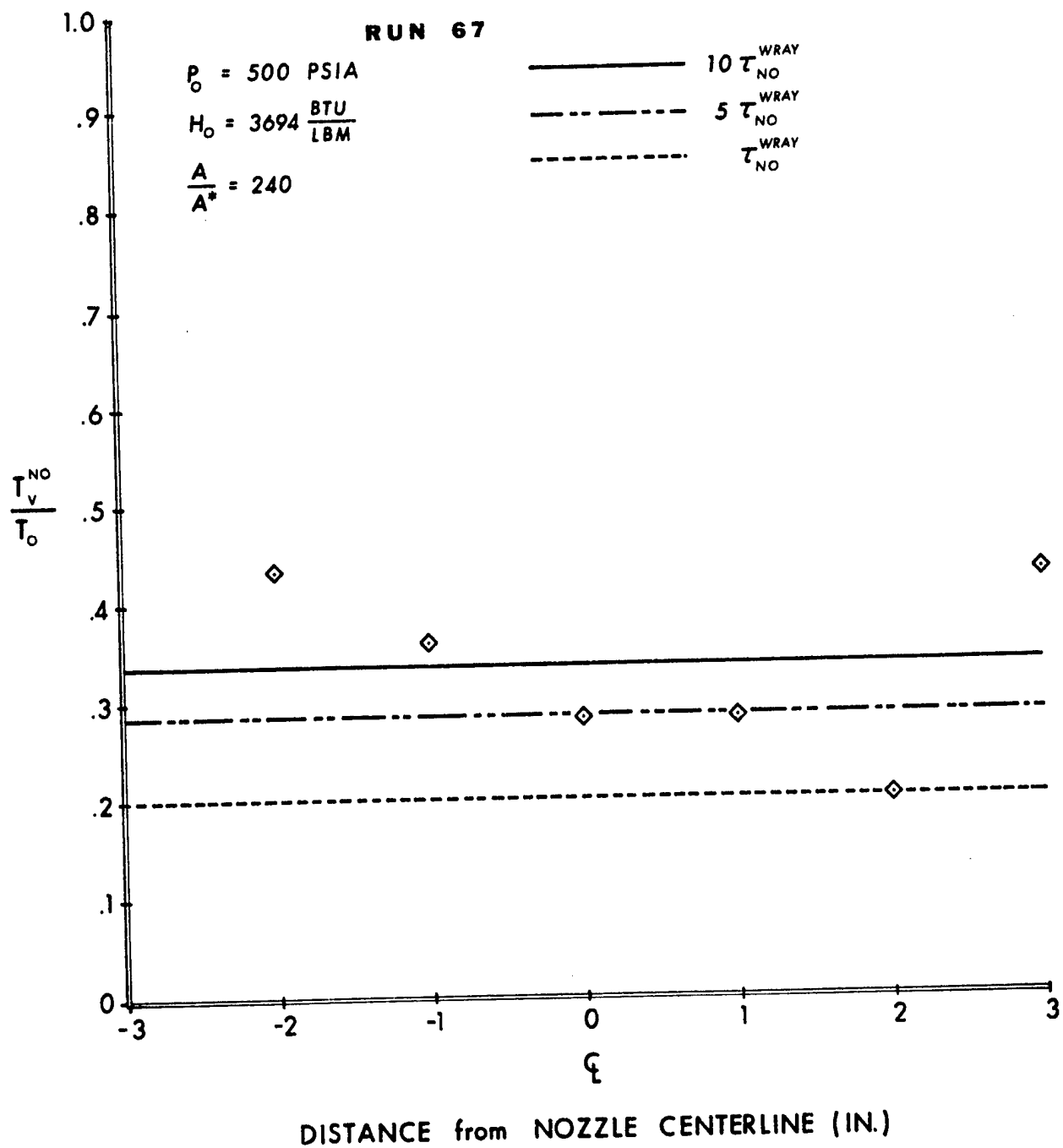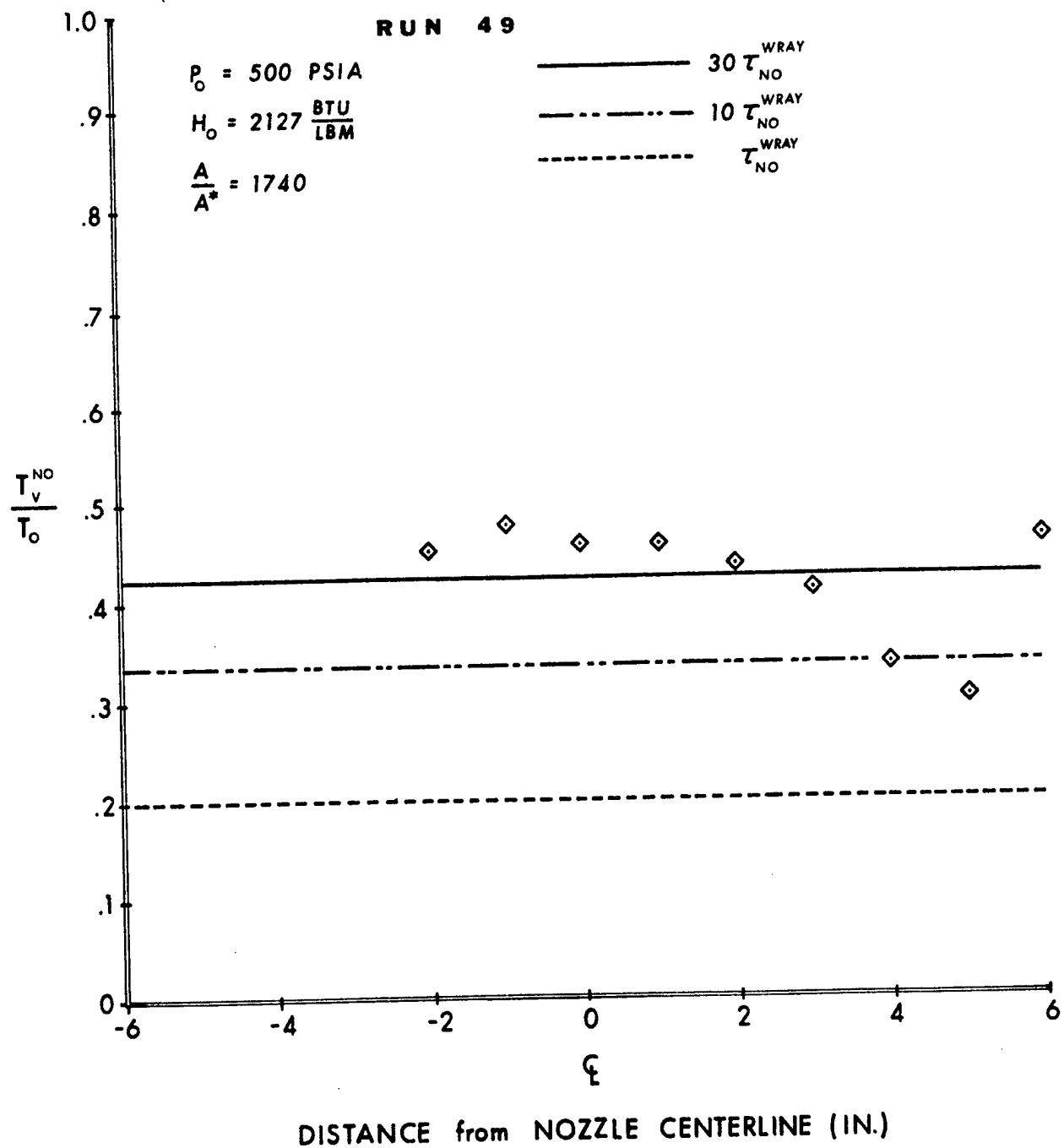
FIGURE 5.   COMPARISON OF NO VIBRATIONAL TEMPERATURE DATA WITH NONEQUILIBRIUM
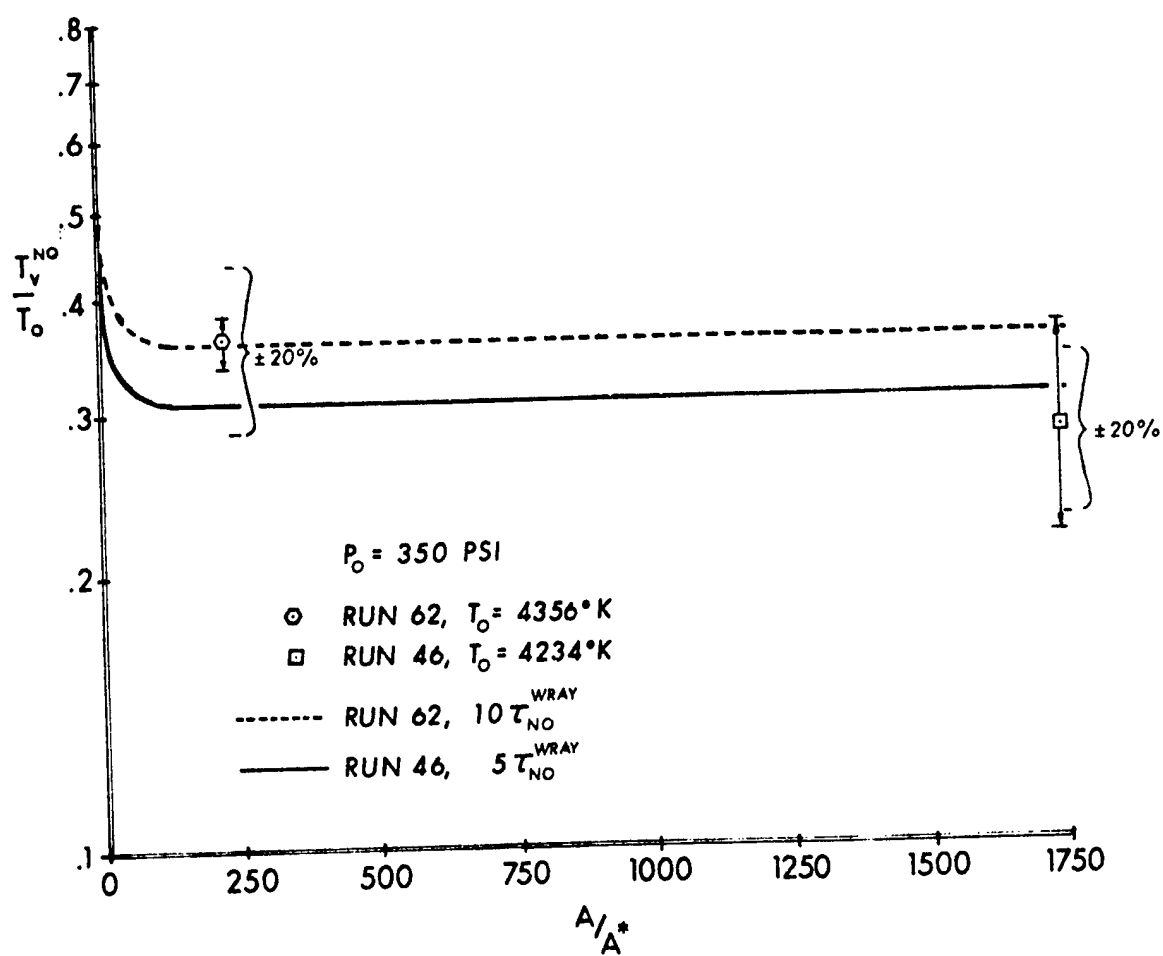CALCULATIONS (T_0 = 3625PK, P_0 = 500 psia, A/A* = 1740)

FIGURE 6. COMPARISON OF AVERAGE VALUE OF TEMPERATURE MEASUREMENTS WITH
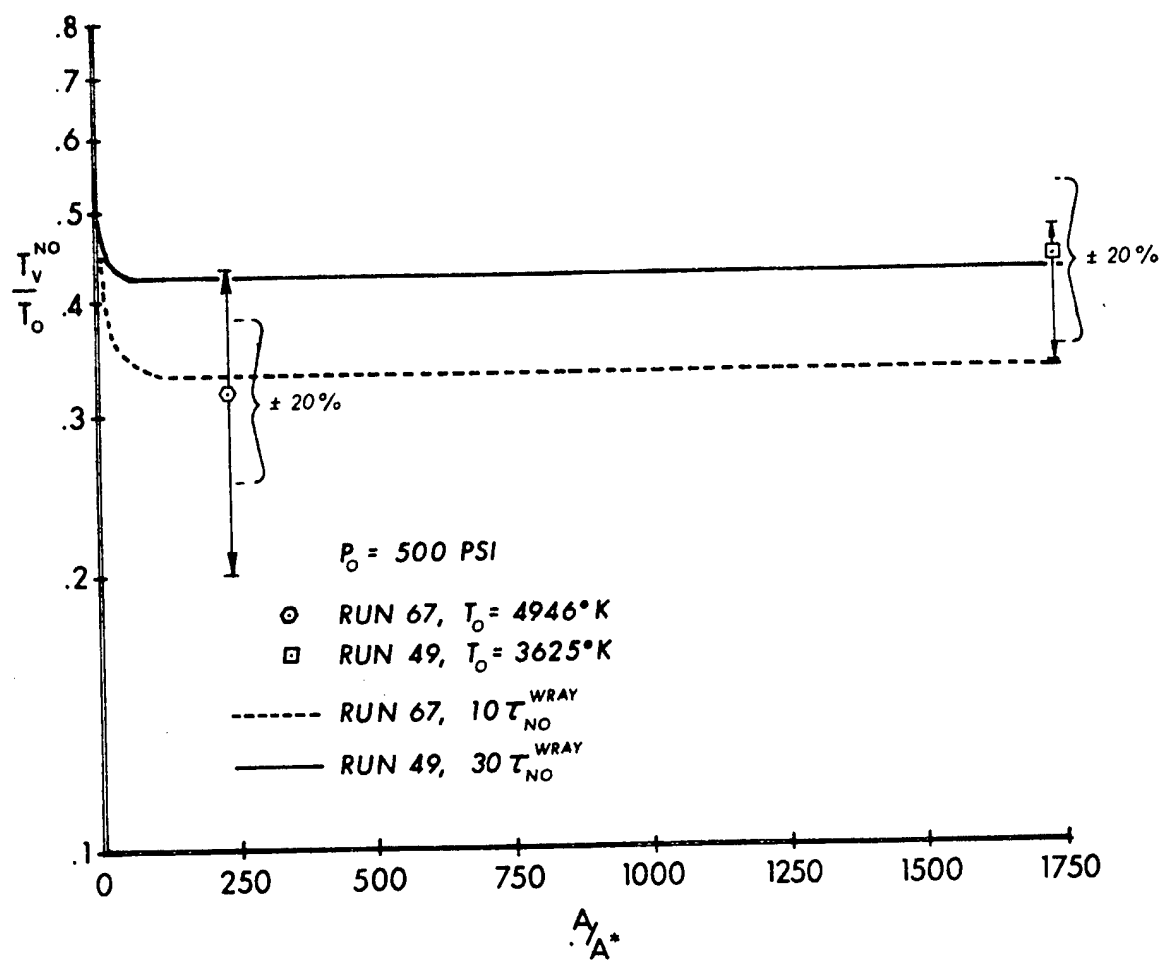BEST VALUES OF THEORY FOR P_0 = 350 psia

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FIGURE 7. COMPARISON OF AVERAGE VALUE OF TEMPERATURE MEASUREMENTS WITH
BEST VALUES OF THEORY FOR P_0 = 500 psia

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with the average value of the measured NO vibrational temperature for each run. Scatter bands about the average values of the temperature show the extreme values of the electron-beam measured NO vibrational temperature obtained for a particular run. Both these limits and the average NO vibrational temperatures were determined by neglecting grossly anamolous points in the inviscid core and those in the nozzle boundary layer. The figures also show the limits of the expected $\pm20\%$ accuracy in the measurement technique. It is seen that the only data within the predicted accuracy was obtained for run 62. Other data was found to have points which fell outside of this range. Hence, more data will have to be taken to determine the experimental accuracy of an average value for the NO temperature for these conditions.

SECTION IV

CONCLUSIONS

Preliminary electron-beam measurements of the vibrational temperature of NO in high enthalpy air expansions are found to be approximately predicted if an NO vibrational relaxation rate between $2.5 \times 10^{-8} \exp[(1.37 \times 10^5/T)^{1/3}]$ and $1.5 \times 10^{-7} \exp[(1.37 \times 10^5/T)^{1/3}]$ is used, i.e., if rates between 5 and 30 times the NO shock-tube rate given by Wray are employed.[8] Because the scatter in these measurements is found to exceed the predicted accuracy of the technique, a more accurate value for a NO relaxation rate cannot be deduced at this time without additional data. A better rate will be obtained with future electron-beam measurements in the 2 Ft EGF.

SECTION V

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